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ABSTRACT (Maximum 200 words)

This study was initiated to determine if and under what conditions supercritical water (SW) would facilitate the removal of heteroatoms (specifically N, Cl and S) from organic compounds. These atoms are representative of those which are present in many hazardous materials which may require efficient methods of disposal. The compounds investigated were: trihexylamine, quinuclidine, benzylidenebenzylamine, quinoline, phenylpiperidine, phenylpyridine, nitrotoluene, dinitrotoluene, ethyl benzilate, cyclohexyl acetate, benzaldehyde, benzyl alcohol, benzyl benzoate, benzoic acid, 1-chlorohexane, 1-chlorododecane, 1-phenyl-3-chloropropane, 2-chlorotoluene, benzyl sulfide and thianaphthene. It was found that some compounds could be converted in good yields to useful materials in SW, particularly with the aid of catalytic additives. This may be a useful alternative to using methods such as oxidation/combustion for their complete destruction. The presence of SW was effective, without the aid of a catalyst, in facilitating the removal of aromatic Cl atoms, which were fairly unreactive under pyrolytic conditions. Finally, the HCl formed from chloro compounds quantitatively reacted with the reactors' metal walls producing hydrogen and metal chlorides.

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**THE REMOVAL OF HETEROATOMS FROM ORGANIC
COMPOUNDS BY SUPERCRITICAL WATER**

FINAL REPORT

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MARCH 14, 1994

U.S. ARMY RESEARCH OFFICE

DAAL03-90-G-0028

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The Removal of Heteroatoms From Organic Compounds by Supercritical Water

FINAL REPORT

STATEMENT OF THE PROBLEM

Since Supercritical Water (SW) has been shown to be effective in removing nitrogen in the form of ammonia from several organic nitrogen compounds (1,2) and in the destruction of cyanide wastes (3), the study of the reactions of SW with organic compounds containing heteroatoms was expanded to include sulfur and chlorine compounds as well as those containing nitrogen with the expectation that it may be effective in their removal also. Specifically, the conditions (primarily temperature) necessary for removal of the heteroatoms and the formation of innocuous organic products were investigated. An acid catalyst (ZnCl_2) or hydrogen transfer agent (dihydroanthracene - DHA) was used when needed. Product distribution and kinetic data were used to elucidate mechanisms for some reactions when possible.

The compounds that were used to model the hazardous materials were divided into four groups:

- (a) Nitrogen compounds - trihexylamine, quinuclidine, benzylidenebenzylamine, quinoline, phenylpiperidine, phenylpyridine nitrotoluene and dinitrotoluene.
- (b) Oxygen compounds - ethyl benzilate, cyclohexyl acetate, benzaldehyde, benzyl alcohol, benzyl benzoate, and benzoic acid.
- (c) Chlorine compounds - 1-chlorohexane, 1-chlorododecane, 1-phenyl-3-chloropropane and 2-chlorotoluene.
- (d) Sulfur compounds - benzyl sulfide and thianaphthene.

SUMMARY OF RESULTS

Nitrogen Compounds

The consumption of p-nitrotoluene was quantitative at all conditions and in the presence of SW gave significantly higher yields of volatile products, primarily p-toluidine and aniline, than the 10-15% obtained from pyrolysis. These higher yields were at the expense of char (solids) and tar (nonvolatile liquid) formation. These volatile product yields were further increased by the presence of 2 Molar ammonia and/or DHA to 40-70% depending on conditions. Ammonia has been found to be an effective catalyst for several SW reactions giving faster reactions and/or more volatile products. Unfortunately, the p-nitrotoluene results were not extrapolatable to 2,6-dinitrotoluene which gave only char and tar, no volatile products, at all conditions.

The compounds quinuclidine and ethyl benzyllate (to be discussed later) were of interest as simulants for BZ (3-quinuclidinyl benzilate). It was thought that trihexylamine could be used as a replacement for quinuclidine since the latter was expensive and difficult to obtain. This proved to be incorrect both because of their relative reactivities and their products. Quinuclidine was fairly unreactive in SW unless the ZnCl_2 catalyst was added (e.g. 100% reacted at 1 hour and 400C with ZnCl_2 vs. 30% at 1 hour and 450C). The main products found were alkyl pyridines which also require a catalyst such as ZnCl_2 to react in a reasonable time period and give complete nitrogen removal.

Quinoline represents the nitrogen heterocycles for which nitrogen removal is more difficult; the product distribution from this reactant had been discussed previously (1). The kinetics of the quinoline - SW reaction, which required ZnCl_2 , led to the following conclusions (4): (a) It is heterogeneously catalyzed with a negligible contribution from homogeneous reactions. (b) The rate is best described by an equation first order in both quinoline and ZnCl_2 and inverse first order in water, which is consistent with a Langmuir-Hinshelwood surface catalyzed, bimolecular mechanism with competitive adsorption between the reactants. The observed activation energy supported this conclusion. (c) The product distribution's dependence on time indicated the initial step in the reaction was the rupture of the CN bond in the 1,2 position, followed by fragmentation of the hydrocarbon side chain to provide species for ring alkylation.

Oxygen Compounds

The results with SW plus ethyl benzilate indicated that the ester portion of BZ would rapidly hydrolyze to form the acid and alcohol as intermediates. The benzilic acid (not observed) decarboxylates quickly to form diphenyl carbinol which further reacts to form primarily diphenyl methane and benzophenone. The addition of ZnCl_2 promoted the further breakdown of these two ring products to give high yields benzene, toluene and ethylbenzene (5). These results lead to the conclusion that the reactions of some hazardous materials with SW could produce chemicals that could be

recycled into commercial products, rather than being completely converted to CO₂ and water by oxidation/combustion methods.

The results with cyclohexyl acetate indicated that the alcohol portion of the ester hydrolysis tends to dehydrate in the presence of SW to form the alkene.

Benzaldehyde was an important intermediate in a previous nitrogen removal study (2). Several of the oxygen compounds examined were either observed or postulated as intermediates also. These compounds confirmed the ability of NH₃ (which would be present during nitrogen removal) to catalyze their reaction, and the results helped elucidated the mechanisms of these reactions (6).

Chlorine Compounds

All the aliphatic chloro compounds reacted similarly whether by pyrolysis or in SW, apparently eliminating HCl rapidly followed by some alkyl chain fragmentation. The most important observation was that in SW the HCl reacted quantitatively with the reactor walls (both Inconel and stainless steel) which was indicated initially by odor and confirmed by Induction Coupled Plasma analyses for metal ions in the water phase. Thus the reaction products could be distorted by the presence of hydrogen rather than HCl, a point which has been overlooked in previous publications (7,8). Attempts to gold plate the steel reactor were not successful due to some of the plating peeling during reaction.

An alternative to be pursued in a new program being initiated is to find conditions at which a glass insert can survive the

pressures in the metal reactor. The approach will be to balance the pressures with water external to the insert and reactant - SW inside the insert. An experiment exposing pyrex, Vycor and quartz to SW showed that pyrex was not suitable, apparently being leached by SW to leave a soft, powdery surface. Vycor and quartz appeared unaffected.

The 2 chlorotoluene was most affected by SW. At 450C and 30 to 60 minutes about 10% reacted during pyrolysis, whereas with SW the reactions were 80-100% complete. The products were about the same in both cases, 40-70% toluene with small amounts of benzene and the rest char and tar. Again the HCl reacted with the walls. Thus, it can be concluded that SW is quite effective in removing aromatic chlorine atoms.

Sulfur Compounds

The compounds were chosen because they represented heterocyclic and aliphatic sulfur compounds which should yield volatile condensable products for analyses. The thianaphthene was quite unreactive, only 20% reacted in 4.5 hours at 500C, yielding small amounts of toluene and benzene the only volatile products found. Thus a catalyst would be necessary for more complete sulfur removal.

The benzyl sulfide was 100% reacted at 400C and 30 min. The major products were toluene and benzene which comprised above 60% of the consumed reactant, small amounts of bibenzyl and a compound with a 180 mass no., possibly dihydrophenanthrene, and traces of biphenyl and a 168 mass no. isomer were found. Unfortunately time

ran out before additional experiments could be performed on these compounds.

PUBLICATIONS

1. Reactions of Organic Compounds With Supercritical Water Involving Chemical Oxidation, by T.J. Houser and C.C. Tsao, Proceedings from the First International Symposium Chemical Oxidation: Technology for the Nineties, Feb. 1991, Technomic Pub. Co., Lancaster, Pa., pp 292-298.
2. Reactions of Supercritical Water With Benzaldehyde, Benzylidenebenzylamine, Benzyl Alcohol and Benzoic Acid, by C.C.Tsao, Y. Zhou, X. Liu and T.J. Houser, J. Supercrit. Fluids, 1992, 5, 107-113.
3. The Removal of Heteroatoms From Organic Compounds by Supercritical Water, by T.J. Houser, Y. Zhou, C.C. Tsao and X.Liu, ACS Symposium Series 514 Supercritical Fluid Engineering Science: Fundamentals and Applications, Eds. E. Kiran and J.F. Brennecke, Nov. 1991, pp. 327-337.
4. Kinetics of the Catalyzed Supercritical Water-Quinoline Reaction, by Zhuangjie Li and Thomas J. Houser, I & EC Res., 1992, 31, 2456-2459.

It is anticipated that the data for some of the results discussed will be published later. If this does occur reprints will be sent.

PARTICIPATING SCIENTIFIC PERSONNEL

Supported personnel:

Thomas Houser - P.I.

Ying Zhou - M.S. Grad. Student

Xu Liu - M.S. Grad. Student

Unfortunately these students have not completed their theses, therefore no degrees have been awarded.

Previous students:

Chung-Cheng Tsao - M.S. Grad. Student

Zhuangjie Li - M.S. Grad. Student

Data obtained by these students prior to the start of the Grant contributed to some of the publications.

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